

Packaging Materials for Thermally Processed Foods in Future Space Missions

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ABSTRACT

Thermally processed shelf-stable foods are important in International Space Station (ISS) programs and essential to the success of future long-duration manned space missions. NASA uses military MRE pouch material to package thermally processed foods for ISS. But the packaging material for MRE pouches contains aluminum (Al) foil as moisture and oxygen barrier. Al foils create potential problem for solid waste disposal in long duration missions, adds much weight, and are not compatible with some of the emerging processing technologies. This is a need to explore the use of non-foil materials that can provide designed shelf-life of 3-5 years for future space missions. This report presents a review on the current status of package options for thermally processes shelf-stable foods and provides an assessment on the potential of using commercially available O₂ and moisture barrier films as a part of package materials for thermally processed foods in future long-duration manned space missions. Based on several criteria, including potential problem in solid waste disposal, weight, mechanical and barrier properties, as well as commercial readiness, laminated EVOH films and SiO_x coated films hold most promise as the future package materials for long-term manned space missions. But as of today, none of the commercial pouch films can provide the required O₂ barrier for 3-5 year shelf-life at ambient temperature. Research is needed to investigate the synergistic effects of better engineered laminated structures, shorter processing times at elevated temperature, and controlled storage conditions to meet the requirements of long-duration space missions, especially missions to Mars.

1. INTRODUCTION

Thermally processed shelf-stable foods are a major component of food supply for International Space Station (ISS) and future long-duration manned space missions. Retorting is the only thermal processing method currently used to produce shelf-stable low acid ($\text{pH} > 4.5$) foods in North America. It is also used by NASA in producing shelf-stable moist foods. Retorting systems rely on convectional surface heating and internal heat conduction to kill anaerobic spores in packaged foods to make them free from pathogenic and most of spoilage bacteria. The high processing temperatures ($120\text{-}130^{\circ}\text{C}$) and relative long processing times (30-60 min) used in those processes cause severe degradation in the processed foods. Emerging food processing technologies that use volumetric heating through microwaves or adiabatic heating though high pressure hold promise to produce high quality shelf-stable foods.

NASA currently uses military MRE pouches for thermally processed foods. But the packaging material for MRE pouches contains aluminum (Al) foil as moisture and oxygen barrier. Al foils create potential problem for solid waste disposal in long-duration manned missions, adds weight, and are not compatible with some of the emerging processing technologies (e.g., microwave sterilization). This is a need to explore the use of non-foil materials to provide 3-5 year shelf-life for future space missions. The objectives of this project were to study the current status of package options for thermally processes shelf-stable foods through a survey of the literature and food package suppliers and provide an assessment on the potential of using commercially available O_2 and moisture barrier films as a part of package materials for thermally processed foods in future long-duration manned space mission.

2. CRITERIA IN SELECTING PACKAGE MATERIALS

To meet the requirements for long-duration space missions, package materials for thermally processed foods need to satisfy the following criteria:

- 1). can be heat sealed and withstand retort temperatures ($120\text{-}130^{\circ}\text{C}$),
- 2). retain adequate mechanical and barrier properties to provide a shelf-life of 3-5 years,
- 3). do not cause problems in solid waste disposal.
- 4). have relatively light weights.

3. PRODUCT SHELF-LIFE

Shelf-life refers to the period of time beyond which the product is no longer acceptable to consumers (Perchonok, 2002). Factors that determine the shelf-life of a food product include microbial growth, chemical reactions (e.g., lipid oxidation, Maillard browning) and physical changes, which are, in turn, influenced by storage conditions, such as temperature, relative humidity and other compositions of the ambient air/gases. The amount of O_2 in packaged foods and/or rate of O_2 ingress into a package are among the most important factors controlling microbial growth and chemical reactions. Different foods have different sensitive to O_2 (see Table 1) with dairy, meat, fish, poultry among the most O_2 sensitive groups. Controlling the O_2 permeability is one of the most important considerations in selecting and designing package materials, especially for shelf-stable foods. Information in Table 1 serves as a general guide for selecting package materials. But in food companies, direct sensory evaluation is often used to determine the shelf-life of shelf-stable products. For example, in Hormel, processed foods are stored at

a pre-determined temperature, and sensory attributes and microbial accounts were evaluated every month. Color, odor, texture, general taste, and/or microbial counts were used as criteria to determine the shelf-life of the products. Hormel's shelf-stable products processed in trays indicate between 12 and 18 month shelf-life.

Table 1. Maximum allowable ingress of O₂ or loss or gain of moisture in shelf-stable products (Armstrong, 2002)

Foods	Max O ₂ ingress, ppm	Max H ₂ O gain (+) or loss (-) %
Canned milk, meats, fish, poultry, vegetables, soups, spaghetti, catsup, sauces	1-5	- 3%
Beer, wine	1-5	- 3%, - 20% CO ₂ or SO ₂
Canned fruit	5-15	- 3%
Dried foods	5-15	+1%
Carbonated soft drinks, fruit juices	10-40	- 3%
Oils, shortenings, salad dressings, peanut butter	50-200	+10%
Jams, jellies, syrups, pickles, olives vinegar	50-200	- 3%

4. OXYGEN BARRIERS

Numerous barrier materials are used in the industry and many are being developed. This section presents a review of several most relevant barrier materials that are or will potentially be used for retortable package materials.

4.1. Polyvinylidene chloride (PVDC)

The copolymer of vinylidene chloride with vinyl chloride was first called Saran by the Dow Chemical Company (Hanlon, 1992). The name, Saran, is now used for any form of polyvinylidene chloride film or coating. PVDC film (normally co-polymerized with 30-50% of vinyl chloride) is soft and transparent. Saran has an excellent barrier properties compared to other films (Table 2), cost about 12 cents per 1000 in². Saran films can be stretched extensive, making them ideal as household wrapping films (thus came the name of Saran Wrap).

Although FDA approves the use of most Saran films as food packaging materials, Japan recently banned PVDC coated films because of suspected negative effects on human health and environment (Jahromi and Moosheimer, 2000). In particular, chlorine presented in PVDC and polyvinyl chloride (PVC) may lead to formation of toxic dioxins on combustion in solid waste disposal (Lange and Wyser, 2003). The solid waste treatment experts at NASA (John Fisher, Lead for Solid Waste Processing Element in Advanced Life Support Division) suggests to avoid chlorinated package materials, and advocate the use of package materials made from high value regenerative elements such as carbon, hydrogen and oxygen in future long-duration manned missions (Email communications with Michele Perchonok, 2004).

4.2. EVOH

Ethylene vinyl alcohol copolymers (EVOH) is a copolymer of ethylene and vinyl alcohol. The structure of EVOH comprises of highly ordered crystalline regions, which provide the high barrier property, and glassy amorphous regions, giving EVOH films flexibility. In a dry state, (EVOH) with 25-45 mole % ethylene are excellent barriers to O₂ (Zhang *et al.*, 2001). A major drawback of EVOH films in food applications is their hydrophilic nature. EVOH absorbs moisture at high relative humidity and in retorting conditions. It was believed that the absorbed water molecules in EVOH interact with the OH groups of the polymer matrix and weakens the hydrogen bonds between polymer chains. This enhances the motion of polymer segments, thus changing the polymer mechanical and barrier properties (Zhang *et al.*, 1999 and 2001).

4.2.1. Glass transition temperature of EVOH

A polymer in a glassy state has better barrier properties than in an amorphous state. When the glass transition temperature T_g of a polymer drops below the storage temperature, the permeability of the package material will increase, thus shortening the shelf-life of stored products. Fully exposed commercial EVOH films with 32-44 mole% ethylene (EF-F15, EF-XL15 and EF-E15 from EVAL) absorb about 3% H₂O (dry basis) at relative humidity (RH), and 6–8% of H₂O in a 100% environment (Zhang *et al.*, 1999). The glass transition temperature of the films drops from 55-62°C to 20°C when the RH increases from 0 to 75%.

4.2.2. O₂ and H₂O permeability of EVOH

Zhang *et al.* (2001) reported that under a given test condition, 15 μ m EVOH films containing 32 mol % ethylene (EF-F15 and EF-XL15) have an O₂ transmission rate (0.2-1 cc/m²-day-atm, depending upon temperature) about 1/7 that of 15 μ m EVOH films with 44 mol% ethylene (EF-E15) in a RH range between 0-60%. The O₂ transmission rate (O₂TR) decrease with RH from 0 to 35% at all three tested temperatures (15, 25 and 35°C), and then slightly increase with RH from 35 to 60%. The O₂TR increases sharply after RH increases beyond 75% which corresponding to a T_g of room temperature for EVOH.

The O₂TR of the biaxially oriented film (EF-XL15) is not different from that of non oriented film (EF-F15) in the RH range between 0 and 60%, while the oriented film has slightly better O₂ barrier properties at higher RH. 15 μ m EVOH films reduced their water barrier property (e.g., 0.3 – 2 g/m² –day-atm, depending on temperature, to 1-10 g/m² –day-atm) as RH increases from 0 to 90% (Zhang *et al.*, 2001).

In a recent report (Kucukpinar and Doruker, 2004) suggests that moisture molecules in EVOH films form hydrogen bonds with the side groups of the EVOH chains and disrupt the hydrogen bonding among the polymers. The increased moisture in EVOH film also enlarges voids among the polymer chains in the amorphous zones. The micro-structure changes lead to increased permeability to water vapor and O₂.

The degree of crystallinity in an EVOH film of a given % mol ethylene can be changed during re-crystallization through orientation and/or heat treatment. For example, for an EVOH film of 32 mol% ethylene, the crystallinity may vary from 27% for a non-orientation film with no heat treatment to 58% with 140°C heat treatment, and to 70% for a biaxial orientation film with 140°C heat treatment. The degree of crystallinity does not

influence O₂ transmission rate (OTR) at 0%RH (0.01 cc-mil/in²-day-atm). But at 100% RH, the OTR decreases from ~3 cc-mil/in²-day-atm to 0.2 cc-mil/in²-day-atm as the crystallinity increases from 25% to 70% (Armstrong, 2000).

4.2.3. EVOH in package materials.

As stated in the above sections, properties of EVOH films are influenced by moisture. In addition to their sensitivity to moisture uptake, EVOH copolymers do not have good compatibility (adhesion and miscibility) with other polar or non-polar polymers (Lagaron *et al.*, 2003). As a result, EVOH films are usually sandwiched by coextrusion in multilayer structures in which the inner and outer layers are hydrophobic polymers, such as polypropylene and PET, for retortable pouches or trays (see table 3). EVOH films may be difficult to laminate and may delaminate during a retort process (personal conversation with Kapak Marketing Director). Special surface treatments were developed to help the adhesion and maintain integrity of the films during retorting processes. Co-extruding EVOH films with other materials may be a less expensive method to produce large quantity of package films (personal conversation with Curwood, WI).

Attempts have also been made to blend EVOH with other polymers. In a recent study, Lagaraon *et al.* (2003) reported on the effect of blending amorphous polyamide with EVOH. The blending did not improve moisture nor O₂ barrier properties, compared with pure EVOH films.

A systematic study on the influence of thermal processing on O₂ ingress in EVOH laminated trays was reported by Zhang *et al.*, (1998). The trays used in the experiments consisted of PP/PE scrap/tie/EVOH (25 µm) /tie/scrap/PP (total 367 µm or 14.5 mil) (200 g capacity) or PP/PE/scrap/tie/EVOH (36 µm/tie/scrap/PP (total 387 µm or 15.2 mil) (256 g capacity). The major findings are: 1) O₂ ingress increased linearly with retorting time – the rate of increase was constant; 2) higher process temperature resulted in high rate of O₂ ingress in package; 3) processing with N₂/62% steam at 121°C resulted in 1/10 of O₂ ingress compared to air/62% steam (~0.001 cc O₂/ min-package vs 0.01cc O₂/min-package); and 4) storage temperature greatly influenced O₂ ingress (e.g., ~0.002cc O₂/day-package at 21.1°C and 60% RH vs ~0.018 cc O₂/day-package at 32.2°C and 75% RH for trays processed at 126°C for 120 min).

EVOH is commonly used in rigid polymeric containers for thermally processed foods. The thickness of retortable pouches (~4 mil) is, however, much smaller than that of rigid containers. The thin PP, PET or nylon films protecting EVOH in those pouch materials would allow large amount water (20-30% of the solid weight of package materials) to be absorbed in EVOH during long retort times. The high moisture content would reduce the melting temperature of the EVOH film, causing it to melt at retorting temperatures. After retorting and upon cooling, EVOH would re-crystallize, expelling the absorbed water. Too tight a material over the EVOH film would cause blisters to form and make the film opaque and degrade the barrier properties. There is a delicate balance in designing retortable EVOH pouch films. The success of using EVOH in pouch materials to a large extent depends upon the thermal processes. EVOH/PP laminated pouch materials are used in commercial applications in Japan, but only used for 3 oz retorted pet foods in the USA (Curwood, MN). According to EVALCAL (Rober Armstrong, July, 2004) the retort times used in the USA is generally much longer than in Japan, making it difficult to meet the requirements. But the parent company of

EVALCAL, Kuraray, has recently developed a retort films (XEF-630) (Table 2) that can meet the shelf-life requirements (1-1.5 year) for most retail products. Kuraray is working on extraction tests before seeking FDA approval of the package materials. New processing technologies such as high pressure and microwave sterilization use much shorter process times. With modification to the current structure of XEF-630 and using the new processing technologies with much shorter process times, it may be possible to produce high quality products with 3-5 year shelf-life.

4.3. Liquid Crystal Polymers (LCP)

Liquid crystal polymers (LCP) are a class of polymers with a high level of crystallinity formed by linear polymer chains (Lusignea, *et al.*, 1999). Polyester is the most used backbone for LCPs. LCPs have unique electric properties: the dielectric properties are constant over a wide range of frequencies and are not sensitive to moisture. This has made LCPs very attractive materials as high frequency substrates in circuit applications. LCPs also have excellent gas and moisture barrier properties. Flodberg *et al.* (2001) listed Vectra A950, a LCP film produced by Ticona, as one of the best barrier polymers at the time of their report. It is a co-polyester consisting of 73 mol% p-hydroxybenzoic acid and 27 mol% 2-hydroxy-6-naphthoic acid, with a density of 1400 kg/m³ and a melting point of about 280°C. Schut (2001) reported on four Ticona Vextran LCP films. From the both reports, it appears that the permeability of LCP films to O₂ and water vapor is comparable to that of dry EVOH film. Schut (2001) also reported that Ticona had developed PP/LCP laminated film for retortable food pouches. It was a single co-extruded PP-tie-LCP (5-10 µm)-tie-PP stiff film, and FDA has given a green light on Feb 21, 2001 for use in USA.

LCPs are expensive. In pure form, the cost of LCP ranged between \$26 and \$33/kg (Lusignea *et al.*, 1999) which is significantly higher than all other polymers, e.g., (~\$1.0/kg, Hanlon, 1992), PET (\$1.3-1.6/kg), PVDC (\$2.8-3.3/kg) and EVOH (~\$4.8/kg) (Osborn and Jenkins, 1992). The high cost of LCP discourages packaging companies from using it for retortable package materials. In addition, Dr. Shepherd from Ticona (personal conversation, 2004) stated that thin LCP films are difficult to handle and tear easily. The laminated structure can help to overcome this problem. But the adhesion for the tie in the laminated structure is relatively weak. Non-traditional adhesions can be used, but obtaining FDA approval of these adhesions can be a daunting task. Because of many technical challenges and shifting of company priorities, some of the earlier active companies in this field, such as Superex Polymer Inc. (Waltham, MA) and Ticona, have decided to stop R&D activities related to LCP in food applications (personal conversation with Jim Shepherd, Ticona, July 23, 2004). The best that Ticona was able to provide WSU was a 10 mil thick film, consisting of HDPE/tie/LCP Vectran V300P (5 µm)/tie/HDPE, which is not suited for retort applications.

4.4. Aluminum foil

Aluminum foil of >0.7 mil is almost impermeable to moisture and gases. Thinner foil has pinholes that make it slightly permeable. The chance of finding a pinhole in size ranging from 0.0000001 to 0.00003 in² in a one ft² foil is about 15% for 0.7 mil and 8% in 1 mil thick foil (Hanlon, 1992), which leads to a moisture vapor transmission rate of 0.03 g/100 in²-day (at 100% RH and 100 F) for the 0.7 mil foil and close to 0 for the 1 mil foil.

Military ready-to-eat meal (MRE) uses aluminum foil of about 0.35 or 0.7 mil thick in a laminated structure (with ~0.5 mil in polyester and 3 mil polypropylene) to provide O_2 and H_2O barrier (see Table 2). The pouches can stand retort temperatures of up to 135°C. The specific weight of MRE foil films is 133 g/m² for the 4 mil thickness film (NASA silver pouch bag) and 163 g/m² for the 6 mil thickness film (NASA brown pouches), which is significantly heavier than 112 g/m² for the 4.1 mil SiO_x coated film (Alcan 17000) and 117 g/m² for the 4.7 mil B-Pack EVOH film (100 μ m PP/EVOH 20 μ m). But most importantly, aluminum foils present difficulty in solid waste disposal for future long-duration manned space missions. There is also a general desire, especially in Europe, to avoid commercial use of aluminum foils because of the difficulty in waste disposal and consumers' perception of high energy use in making aluminum foil (Lange and Wyser, 2003).

Packaging films containing aluminum foil or a metalized layer of polymer film are not suited for microwave sterilization because the metal sheet prevents electromagnetic energy from penetrating into the packaged foods. High pressure processes can compromise the integrity of those materials. For example, visible signs of delamination were observed between the polypropylene (PP) and aluminum (Al) layers in MRE pouches processed at >200 MPa at 90°C (Schauwecker *et al.*, 2002). High pressure processes (600-800 MPa for 5-10 min at 40-60°C) also caused structure damages to metalized PET films (Caner *et al.*, 2003) and significantly reduce barrier properties of those package materials (Caner *et al.*, 2000).

4.5. Silicon Oxide (SiO_x) Coating

Early development of high barrier coated polymeric films started in 1959 with aluminum metallization techniques. In 1980's, transparent SiO_x coated films were developed as alternatives to metalized plastics (Leterrier, 2003). Similar to aluminum metallization, deposition of a thin layer of low permeability SiO_x on a thermoplastic substrate sharply improves barrier properties. Many deposition methods have been developed over the years, including sputtering, electron-beam deposition and plasma-enhanced chemical vapor deposition (PECVD) (Erlat *et al.*, 2000). PECVD was developed in early 1990s and used extensively in the microelectronics industry to deposit silicon dioxide on thin films as electric insulation. It can deposit SiO_x below the glass transition temperature of the substrate polymers and has the advantages in adhesion and step coverage of silica coating. This makes the silica coating more flexible and resistant to cracking during the converting processes, namely lamination printing and making pouches for food applications (Teshima *et al.*, 2003).

Typical thickness of the SiO_x is between 10-50 nm, and the polymer substrate between 12 and 25 μ m. Thicker layer becomes brittle (Hedenqvist and Johansson, 2003). The permeability of these laminated films for O_2 is about 0.3-0.5 cc/m²–day–atm, which is very low compared to that for most polymer films, but still several order of magnitude higher than that of silica glass (Roberts *et al.*, 2002). Many papers suggest that defects exist in the coating, creating pathways for O_2 . A recent study has found that gas permeates directly through oxide matrix, suggesting a quite different lattice structure of SiO_x than annealed silica glass, with the former being a more open structure (Erlat *et al.*, 2000). Roberts *et al.* (2002) used mathematical models to study the influence of three different possible types of defects, namely macro (>1nm), nano (0.1-1 nm) and lattice

(0.2-0.3 nm), on permeability of O₂. Their study indicates the presence of macro-defects, but those defects are small and rare, and could not be detected by atomic force microscopy (AFM). ATM images show clearly irregular surface array of columnar grain-like structures likely caused by growth around isolated nucleation centers during the coating in a vacuum deposit coater.

The SiO_x coat is, however, fragile. Hedenqvist and Hohansson (2003) studied the effects of 90 degree folding of SiO_x coated films and found that 1-2 times folding initiated cracks in the coating and increased O₂ permeability by 13-74 %. Preliminary tests in my laboratory show that the O₂ transmission rate of the films increased four times after retorting, from 1.2 cc/m²-day-atm to 5.0 cc/m²-day-atm (Table 2). Packaging companies have also expressed concern with regard to the converting processes (making laminated package materials from the films) in that cracks may develop. For example, the economic losses might be very large, if 0.5 million pouches are produced with defects that are not detected (personal conversation with CURWOOD representatives).

4.6. AlO_x and AlO_xN_y Coating

Thin transparent Aluminum oxide coatings are also used to improve barrier properties of package films. Recent studies (Erlat *et al.*, 2004) have shown that inclusion of nitrogen in AlO_x coating offers a significant improvement of O₂ and H₂O properties in those films. However, the plasma enhanced chemical vapor deposition (PECVD) coating method commonly used for AlO_x and SiO_x requires the use of silane as a precursor, which makes it unattractive in commercial production of the films. Erlat's group at Oxford University developed a reactive magnetic sputtering method to overcome the difficulty. The O₂ transmission rate for the PET (50 μm)/AlO_xN_y films decreased from ~50 cc/m²-day to 1 cc/m²-day as the coating thickness increased from 0 to 80 nm (Erlat *et al.*, 2004). The still relatively high O₂ transmission rates were attributed to a significant numbers of micron-scale defects that provide permeation pathways through the films. Water vapor transmission rate decreased from 1 g/m²-day to 0.1 g/m²-day, as the coating thickness increased from 20 to 80 nm.

AlO_x coated films suffer from the same fragility problem as SiO_x coated films. A recent study at Illinois Institute of Technology shows that the O₂ transmission rate increased from 0.54 cc/m²-day-atm to 25 cc/m²-day-atm after a high pressure process (preheated to 90°C, and processed at 688 MPa), a 46 fold increase (Table 2).

4.7. Nanocomposites

Nanocomposite films incorporate nano particles, typically 100-1000 nm, in a polymer matrix to increase tortuosity of diffusion pathway and, thus, increase barrier properties (Lange and Wyser, 2003). Those particles can be inorganic clays or LCP. The difficulty of making those films lies in dispersion of those particles in the matrix and difference in their melting points. To the best of the author's knowledge, noncomposite films not are used in commercial food applications.

Table 2. Properties of commercial package films/trays

Barrier	Film description	O ₂ Transmission Rate (cc/m ² -day) Before Retort	O ₂ Transmission Rate (cc/m ² -day) Post Retort	H ₂ O Transmission Rate (gm/m ² -day)	Description of the films outside -- inside	Source of information
EVOH	Combitherm	0.51, measured at 24 C and 50% rh	Process condition: 121C and 30 min	3.1	Nylon/EVOH/nylon/LF adhesive/HV PE/LLDPE	NASA Food Lab
	B-Pack Film	≤ 0.7, measured at 23 C and 0% rh		<15, measured at 38C and 90% R.H.	PP/PA/EVOH retortable 10 micron/PA/PP	B-Pack, S.p.A.-Italy
	Eval XEF-630 -- new product (May, 2004)	0.3 at 20C and 85%	0.4 -- after retort at 120C and 30 min with water		Barrier/ Ony (0.6mil)/CPP (2.0 mil)	Kuraray, Con., LTD, EVAL Company
SiOx	Alcan 17000	<1.55		<2.33		Alcan specification
	Alcan 17000	1.2	5.0		Polyester (0.48 mil)-SiOx (0.6) - PP (3)	Juming Tang, WSU
AlOx	Pyramid 4381	0.54	25 (post high pressure process)		N/A	Tiariana N. Koutchma, IIT
LCP	Vectra A950					Film from Ticona, data by Flodberg <i>et al.</i> , 2001
	Time in compression moulding					
	8 min	0.45 (6.5 mil thick)				
	30 min	0.2 (5.4 mil)				
Foil Pouches	MRE	0.06		0.01	N/A	Natick

5. EMERGING PROCESSING TECHNOLOGIES

Over the past five years, major processing technology developments have been supported by the US Army Natick Soldier Center and US Department Defense to provide high quality shelf-stable foods for the military. The required shelf-life for shelf-stable military rations is three years at 80°F (26.6°C). This is not much different from the requirement for NASA long duration mission programs. The two most promising technologies for shelf-stable food products for long- duration manned space missions are: 1) 915 MHz Single Mode Microwave Sterilization Technology; 2) High Pressure/Thermal Processing Technology. The following sections provide brief introductions to these two technologies and their affect package barrier properties.

5.1. WSU 915 MHz Microwave Sterilization Technology

Microwave heating is a result of the polarization effect of electromagnetic radiation on foods at frequencies between 300 MHz and 300 GHz. Microwaves can interact directly with foods to generate heat in hermetically sealed polymeric containers. Microwave sterilization has an advantage over retorting of canned foods because of the short heating time and potential for more uniform heating. Commercial microwave sterilization

processes are now used in Belgium (Tops Foods, Belgium) and Japan (Otsuka Chemical Co., Osaka, Japan). Products from Tops Foods and Otsuka Chemical Co. demonstrate that microwave sterilized products containing pasta, rice, and meats have better organoleptic quality and appearance than frozen products.

No commercial microwave sterilization systems are used in North America. The 2,450 MHz microwave sterilization technology used in commercial applications in Europe and Japan could not be adopted in the USA due to more stringent FDA requirements. A major technical problem with the 2,450 MHz microwave systems is the unpredictable cold spot in the food packages. As a result, the processed foods require 100% incubation before being released to market. To overcome this problem, the Advanced Thermal Processing Technology Team at Washington State University (WSU) used 915 MHz microwave and developed signal-mode sterilization concept (Pathak *et al.*, 2003). The WSU design combines microwave heating with circulating water at 121°C to shorten process time (Guan *et al.*, 2002). A Microwave Sterilization Consortium was formed in 2001 with support from the US Department of Defense Dual Use Scientific and Technology (DUST) Program, Washington State University and its industrial partners. The aim of this consortium is to develop and scale-up the 915 MHz single-mode microwave sterilization technology for industrial processing of shelf-stable package foods for military and civilian uses. WSU Microwave Sterilization Consortium consists of US Army Natick Soldier Center and eight companies, including Kraft, Masterfoods, Hormel, Ocean Beauty Seafoods, Truitt Brothers, Rexam Container, Graphic Packaging, and Ferrite Component. The Technical Service Center of National Food Processors Association (Dublin, CA) serves as a technical advisor on microbial safety and FDA approval. Over the past three years, the consortium has addressed several major technical issues, including developing a pilot-system for demonstration and engineering studies, developing techniques for locating cold spots in packaged foods (Lau *et al.*, 2003), monitoring temperature during MW processes and microbial challenge studies (Guan *et al.*, 2003). Our newly developed pilot-scale system can complete a thermal process for 7 oz trays ($F_0 = 6$) in 5-8 min, a significant reduction in processing times compared to the conventional processes of approximately 30 min. With the system, the WSU team and industrial partners tested on some heat sensitive products that could suffer significant quality losses in conventional retort systems (e.g., Guan *et al.*, 2002). The new technology shows promises for producing very high quality fish, dairy, pasta, and meat products. During the June 22-23 2004 consortium meeting at WSU, the consortium decided that we are ready to contact FDA in developing approval documents and that we should move ahead to scale-up the processes for industrial applications. It may still take approximately 2-4 years before commercial application of FDA approved industrial systems. But the WSU pilot-scale system, designed to mimic industrial operations, is available for product and packaging feasibility studies.

MRE foil pouches shields electromagnetic fields from reaching food in packages and, therefore, are not suited for microwave sterilization processes. At Washington State University, we use pouches made of SiO_x coated films or polymeric trays with EVOH barrier and Seran based lid stock. The O_2 transmission rate for both the Seran based lid stock and the SiO_x coated films after the post process is approximately 2 cc/m²-day (Table 2). Rexam Containers and EVALCAL are very excited about the short process times (5-8 min) when using our microwave sterilization system in connection with

EVOH package films. Two unique design features of the WSU Microwave Sterilization Technology offer opportunities to maintain the integrity of EVOH based films: 1) water immersion during the MW heating reduces the partial pressure of O₂ and thus reduces the gas ingress; 2) the short exposure times of food packages reduces moisture migration into package materials and, thus, eliminates the problem associated with melting down of soaked EVOH films.

5.2 High Pressure Process (HPP)

High pressure processes (HPP) refer to a novel food preservation technology that uses high pressures >300 MPa to inactivate pathogenic and spoilage micro-organisms in foods. HPP is effective in inactivating most vegetative pathogens, and are now used worldwide in commercial operations to extend the shelf-life of many commodities, including orange juice, avocado pulp, sliced ham, meats, oyster, salsas, and guacamole. A major advantage of HPP is that it does not rely on thermal energy or use little thermal energy to inactivate most of food pathogens, thus help to retain most quality attributes of the processed foods. HPP sterilization for low-acid (pH>4.5) foods is still under development (Sizer *et al.*, 2002), because HPP alone is not adequate in inactivating spores that pose great risk in low-acid shelf-stable foods. Current research and development activities related to HPP sterilization processes relies on the adiabatic heating of foods via high pressure from a relatively high initial product temperature (e.g., 90°C) to a final temperature of 121°C (Morris, 2001). This process is commonly referred to as a thermally-assisted HPP process. Several technique issues remain to be addressed before HPP sterilization processes can be approved by FDA and implemented by the food industry: 1) selection of the most resistant food pathogen spore as the target bacterium to design a HPP process; 2) selection of a surrogate that is non pathogenic micro-organism and more resistant than the target bacterium for process development and validation; and 3) identification of the least treated location in foods during HPP processes for process development.

In order to speed up the technology development of HPP sterilization technology for low acid foods, a consortium led by US Army Natick Soldier Center was formed in 2000 with support from the DoD Dual-Use Scientific and Technology Program. Two active consortium members are the National Center for Food Safety and Technology at Illinois Institute of Technology (Summit-Argo, ILL) and Avure, a subsidiary of Flow International (Kent, WA). In addition, the National Food Laboratory of National Food Processors Association serves as a subcontractor for the microbial studies and is conducting a research to study the kinetics of *C. botulinum* spores under HPP conditions. It is anticipated that the HPP Consortium will be ready by the end of 2004 to approach FDA in preparation for petition document (personal email communication with Dr. Pat Dunne, US Army Natick Soldier Center, MA). HPP is suited for food products that have little air voids and do not undergo undesirable texture changes under high pressure.

Delamination is often observed in MRE foil pouch materials after HPP, while transparent SiO_x coating fractures and becomes translucent under pressure. Laminated EVOH films are not affected by HPP in pasteurization processes and are currently used for many HPP pasteurized foods, including guacamole (personal communication with Rober Armstrong, EVALA, TX).

Table 3 summarizes advantages and limitation of the films discussed in this section.

6. SUMMARY AND DISCUSSIONS

The technologies for LCPs and nano-clay/polymer films are still immature to allow the use of those films as food packages in long-duration manned missions. There are significant technical hurdles to be overcome, and it is difficult to predict when some of those films may be commercially available for retort applications. There appears to be large momentum in developing transparent films coated with SiO_x, Al₂O₃ or TiO₂ to provide unique barrier properties. Films of this type are commercially available, but can still not meet the NASA requirements in terms of post-process barrier properties. EVOH films in laminated structures appear to be most promising in providing the required shelf-life for packaged products. In addition, EVOH films contain basic elements of C, O and H, all of high regenerative in space missions, and can serve as a source for recovery of O₂ and water.

MRE pouches currently used in NASA and the US Army can hold 8 oz (226 g) moist products. An 8 oz capacity pouch has approximately 0.052 m² surface area. The upper limit for the maximum allowable O₂ in most sensitive food category (e.g., fish, meat, dairy, and poultry) is 5 ppm which corresponds to about 0.8 cc of O₂ at standard conditions (Table 1). For a 3 yr (1092 days) self-life, the maximum rate of O₂ ingress into the package should be less than:

$$O_{2,ir} = \frac{0.8cc}{1092day * 0.052m^2} = 0.014cc/m^2 - day$$

The transmission rate for package materials should be less than:

$$OTr = \frac{O_{2,ir}}{\Delta P_{O_2}}$$

where, ΔP_{O₂} (in atm) represents the difference in partial pressure of O₂ across the package material. In dry atmospheric air, ΔP_{O₂} is 0.2095 atm. This value is reduced in humid air. So for a conservative estimation, we would require that the package material provides an OTr of 0.067 cc/m²-day-atm (0.0043 cc/100 in²-day-atm).

It is clear from the above calculation and Table 2 that none of the current non-foil package materials meet the requirements. It may, however, be possible to use the synergistic effects of good processing technologies (shorter processing times) and right storage conditions (reduced partial pressure of O₂ and controlled temperature) to enhance the performance of EVOH laminated package materials (and thicker barrier films) to provide 3-5 year shelf-life for thermally processed products.

Table 3. Summary of options of package materials in future space missions

Package material	Mechanical properties	Environmental	Barrier property	Commercial readiness	Compatible with MW and HHP
Foil/metalized	Good	Poor	Good	Good	Poor
PVDC	Good	Poor	Fair	Good	Good
EVOH	Good	Good	Fair	Fair	Good
SiO _x coated	Poor-fair	Good	Fair	Fair	Poor-fair
LCP	Poor	Good	Good	Poor	N/A
Nano	N/A	Fair	N/A	Poor	N/A

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ATTPENDIX

Definitions/Equations

Transfer of mass through a package film can be described by the following equation (Brody, 2003):

$$\frac{dM}{dt} = \frac{k}{l} A \Delta P \quad \dots (1)$$

where, M is the mass or volume of a gas transmitted through the film (g or cc), t is time (day), k is the **permeability** of the film material for the gas under consideration (cc-mil/m²-day-atm), A is the area of the film (m²), l represents the thickness of the film (mil), and ΔP is the difference in partial pressure of the gas across the film (atm). In our ambient environment, ΔP is 0.209 for O₂ and 0.0003 for CO₂ (Brody, 2003).

Transmission rate, Tr (cc/m²-day-atm), is defined as:

$$Tr = \frac{k}{l} \quad \dots (2)$$

From Eq. (2):

$$k = Tr \times l \quad \dots (3)$$

Permeability reflects the intrinsic barrier property of one material, while transmission rate represents the barrier property of the film. The latter is inversely proportional to the thickness of the film (see Eq. 2).

Calculation of O₂ mass from volume:

Molar mass of O₂ is 32, 1 mole of an ideal gas at 1 atm and 20 °C is ~22,400 cc. So 32g O₂ occupies 22,400 cc volume.

The maximum allowable O₂ in most sensitive foods is 5 ppm (Table 1). The maximum allowable volume of O₂ in a 200 g food package is thus:

$$V_{O_2} = \frac{5 \times 10^{-6} * 226g * 22,400cc}{32g} = 0.79cc$$